

On the Osmotic Pressure of Compressible Solutions of any Degree of Concentration. Part II. Cases in Which Both Solvent and Solute are Volatile

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On the Osmotic Pressure of Compressible Solutions, etc. 457

The main results of the research may be summarised as follows :—

(a) From the dilatometric and crystallographic work no definite information is forthcoming which affords any precise proof as to a difference in properties of the two tetragonal modifications of ammonium nitrate.

(b) The argument derived from the investigation of the thermal properties tells, so far as it goes, against the identity of the two tetragonal modifications, but it cannot be considered as decisive.

In conclusion, I desire to express my thanks to Professor Arthur Schuster for placing at my disposal the resources of the physical laboratory of the Manchester University.

On the Osmotic Pressure of Compressible Solutions of any Degree of Concentration. Part II.—Cases in which both Solvent and Solute are Volatile.

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(Communicated by Professor F. T. Trouton, F.R.S. Received January 30,—
Read February 20, 1908.)

In a former paper (to be referred to here as Part I) which appeared in the 'Proceedings of the Royal Society,'* I found an exact relation between vapour-pressures and osmotic pressure in the usual case in which the solute may be taken as involatile. The case now to be considered is the more general one in which both solvent and solute are volatile. The concentration and temperature in the main part of the paper are taken as constant; and the only restriction upon them is that the solutions and solvent must be capable of existing in the liquid form. The notation employed is the same as in Part I, any additional symbols being specially defined when they occur.

1. I shall make use of the general theorem, proved in Part I, that when a solution is in osmotic equilibrium with the pure solvent, the vapour-pressure of the solution is equal to the vapour-pressure of the pure solvent, each measured for the actual hydrostatic pressure of the fluid to which it refers; that is, with the former notation :

$$\pi_p = \pi_{0p_0} \quad (1)$$

This was shown to be true whether the solute is volatile or not.

* A, vol. 79, 1907, pp. 519, *et seq.*

458 Mr. A. W. Porter. *On the Osmotic Pressure of* [Jan. 30,

2. I shall utilise the formula giving the dependence of the vapour-pressure of the pure solvent upon hydrostatic pressure, viz. :—

$$\int_{p_0'}^{p_0} u dp = \int_{\pi_{0p_0'}}^{\pi_{0p_0}} v dp,$$

or, inserting the equality (1),

$$\int_{p_0'}^{p_0} u dp = \int_{\pi_{p_0'}}^{\pi_{vp_0}} v dp. \quad (2)$$

The upper limits, which may be any corresponding values, shall be taken as

$$p_0 = \pi_{00} \quad \text{and} \quad \pi_{0p_0} = \pi_{00}.$$

3. Let now an isothermal cycle of operations be performed upon a large (practically infinite) mass of solution at a pressure p in osmotic equilibrium with the solvent under a pressure p_0 . The sum of the external works done in the various stages of the cycle will be equated to zero. Let the solution

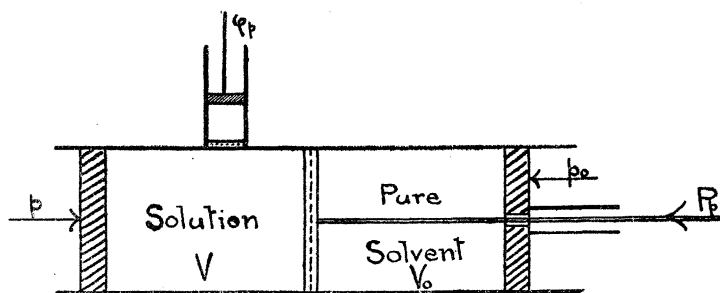


FIG. 1.

contain c grammes of solute to each gramme of solvent, the solute being defined as the constituent to which the membrane is impermeable. (In other respects it would, of course, be a matter of indifference as to which was considered to be solvent and which solute.)

Stage (a).—Force 1 gramme of the solvent out of the solution osmotically, letting the vapour of c grammes of the solute simultaneously escape into the lateral cylinder through a membrane semi-permeable alone to the vapour of the solute which is at a pressure ϕ_p . The work done upon the system in this two-fold change is

$$(1+c) P_p \sigma_p - p_0 (u_{p_0} - (1+c) \sigma_p) - \phi_p c w_p,$$

where w_p is the specific volume of the solute-vapour when in equilibrium with the solution under a hydrostatic pressure p , σ is the specific volume of the solution, and the other quantities have their previous meanings.

Stage (b).—Increase the pressure of the vapour thus formed to $\phi_{p'}$, simultaneously increasing the hydrostatic pressures of the solution and the solvent to the corresponding equilibrium values p' and p_0' respectively. The work done upon the system in this stage is

$$-c \int_{\phi_p}^{\phi_{p'}} \phi dw - \int_p^{p'} p d(V - (1+c)\sigma) - \int_{p_0}^{p_0'} p_0 d(V_0 + u_{p_0}),$$

where V and V_0 are the original volumes of the solution and the solvent.

Stage (c).—Restore the gramme of the solvent osmotically to the solution and simultaneously force in the c grammes of the solute-vapour from the lateral cylinder. The corresponding work is

$$-(1+c)P_p\sigma_{p'} + p_0'(u_{p_0'} - (1+c)\sigma_{p'}) + c\phi_{p'}w_{p'}.$$

Stage (d).—Compress both the solution and the solvent to their original volumes and pressures. The work done is

$$-\int_{p'}^p p dV - \int_{p_0'}^{p_0} p_0 dV_0.$$

Each of these stages is reversible and isothermal, and the total work done must thence be zero. The sum, after integration by parts and simplification, is

$$(1+c) \int_{p'}^p \sigma dp = \int_{p_0'}^{p_0} u dp + c \int_{\phi_{p'}}^{\phi_p} w dp. \quad (3)$$

Now, the lower limits may be any equilibrium values, and we shall take them to be

$$p' = (\pi + \phi)_{(\pi + \phi)}, \quad \phi_{p'} = \phi_{\pi + \phi}.$$

These values of p' and $\phi_{p'}$ are respectively the pressure of the solution when in contact with the vapours of its constituents alone, and the corresponding pressure of the vapour of the solute.

4. Add together formulæ (2) and (3);

$$(1+c) \int_{(\pi + \phi)_{(\pi + \phi)}}^p \sigma dp + \int_{p_0'}^{\pi_{00}} u dp = \int_{p_0'}^{p_0} u dp + \int_{\pi_{p'}}^{\pi_{00}} v dp + c \int_{\phi_{(\pi + \phi)}}^{\phi_p} w dp;$$

or, since

$$\pi_{p'} = \pi_{(\pi + \phi)},$$

$$(1+c) \int_{(\pi + \phi)_{(\pi + \phi)}}^p \sigma dp = c \int_{\phi_{(\pi + \phi)}}^{\phi_p} w dp + \int_{\pi_{00}}^{p_0} u dp + \int_{\pi_{(\pi + \phi)}}^{\pi_{00}} v dp. \quad (4)$$

This is the formula desired; the osmotic pressure is $P_p = p - p_0$.

The connection between this formula and the more restricted one previously given is not immediately obvious. By considering a cycle in which, as in

460 Mr. A. W. Porter. *On the Osmotic Pressure of* [Jan. 30,

Part I, 1 gramme of the solvent is allowed to escape through the osmotic membrane, and the c grammes of the solute are allowed to remain in the solution (which must be considered to have a practically infinite volume), the remainder of the cycle being conducted as above, I obtain the alternative expression

$$\int_{(\pi+\phi)(\pi+\phi)}^p sdp = \int_{\pi_{00}}^{p_0} udp + \int_{\pi(\pi+\phi)}^{\pi_{00}} vdp, \quad (4')$$

where s denotes the *shrinkage*, that is, the reduction of the practically infinite volume of the solution when 1 gramme of the solvent escapes; *i.e.*, $\left(\frac{\partial V}{\partial m_1}\right)_{m_2}$, where m_1 and m_2 denote the masses of the solvent and solute.

Comparing these two results, we see that

$$\int_{(\pi+\phi)(\pi+\phi)}^p sdp = (1+c) \int_{(\pi+\phi)(\pi+\phi)}^p \sigma dp - C \int_{\phi(\pi+\phi)}^{\phi_p} wdp.$$

This is an interesting connection between the shrinkage and the specific volume of the solution. Differentiating with respect to p , we obtain the equation

$$s_p = (1+c) \sigma_p - cv_{\phi_p} \frac{\partial \phi_p}{\partial p}. \quad (5)$$

The meaning of this equation will be examined in Section 6.

5. The above results have been obtained by making $\Sigma \int p dv$ round a reversible isothermal cycle equal to zero. But round such a cycle it is equally true that $\Sigma \int v dp$ is zero. The separate terms in this summation can be written down at once for the same cycle that has been considered. The result is the general equation (4) *without any further reduction*.

6. The mode of variation of vapour-pressure with the hydrostatic pressure to which the liquid is subjected can be determined by a slight modification of the method in Part I. The sole change required is that the liquid in the cylinder be enclosed by two pistons, the inner one of which is permeable to the vapour of the solvent, but impermeable to the vapour of the solute; the second piston must be impermeable to both. If the inner piston is maintained permanently in contact with the surface of the solution, none of the solute evaporates. The changes that proceed in the cycle considered are, therefore, precisely the same as for the case of an involatile solute, and the equation for the change of the vapour-pressure of the solvent with hydrostatic pressure comes out the same as before. Since each constituent may in turn be considered as the sole volatile one, a similar equation applies to each.

Hence we obtain

$$\partial\pi_p/\partial p = s_p/v_{\pi_p},$$

as before, and similar equations for the vapour-pressure of each of the other constituents present.

In each case $s_p = \partial V/\partial m$, where V is the total volume of the solution and m is the mass of the particular constituent to which s_p refers.

Examining equation (5) in the light of these results, we see that since $s_p = \left(\frac{\partial V}{\partial m_1}\right)_{m_2}$, where m_1 = mass of *solvent* present in the volume V ; and $\omega_{\phi p} \frac{\partial \phi_p}{\partial p} = \left(\frac{\partial V}{\partial m_2}\right)_{m_1}$, where m_2 is the mass of the solute, the equation becomes

$$\left(\frac{\partial V}{\partial m_1}\right)_{m_2} + c \left(\frac{\partial V}{\partial m_2}\right)_{m_1} = (1+c) \sigma_p = V, \quad (6)$$

and this is mathematically equivalent to the statement that σ_p is a function of c , that is of m_2/m_1 : a statement which of course is true.

7. The equation (4) is easily extended to the case where there are any number of volatile solutes present. It becomes

$$(1 + \Sigma(c)) \int_{[\pi + \Sigma(\phi)][\pi + \Sigma(\phi)]}^p \sigma dp = \Sigma c \int_{\phi\pi + \Sigma(\phi)}^{\phi p} w dp + \int_{\pi\pi}^{p_0} u dp + \int_{\pi\pi + \Sigma(\phi)}^{\pi\pi} v dp,$$

where the terms referring to the solvent are kept separate from the rest, because, owing to the special character of the osmotic membrane, the solvent is on a different footing from the other constituents.

When the solution is under the hydrostatic pressure of the vapours of its constituents alone, this equation reduces to the exceedingly simple one,

$$\int_{\pi\pi}^{p_0} u dp + \int_{\pi\pi + \Sigma(\phi)}^{\pi\pi} v dp = 0.$$

This can be represented (as in Part I) on the indicator diagram of the pure solvent.

8. To find the variation of osmotic pressure with hydrostatic pressure, differentiate (4) with regard to p :

$$(1+c) \sigma_p = c w_{\phi p} \frac{\partial \phi_p}{\partial p} + u_{p_0} \frac{\partial p_0}{\partial p} = c w \frac{\partial \phi_p}{\partial p} + u_{p_0} \left(1 - \frac{\partial P}{\partial p}\right).$$

By (5) this is equivalent to

$$s_p = u_{p_0} \left(1 - \frac{\partial P}{\partial p}\right).$$

Hence the variation of the osmotic pressure with the hydrostatic pressure of the solution is given by the same equation as for the case where the solute is involatile.

9. The theorem that the vapour-pressure of the pure solvent increases with the hydrostatic pressure can be obtained in a very simple way as follows :—

Let a vertical tube containing the solvent be enclosed in a closed chamber in a *gravitational field*, and let equilibrium be set up. Let now membranes permeable to the vapour alone be inserted in the side of the tube at a distance apart dh . Let p_0 be the hydrostatic pressure in the liquid at any point, and π_{0p_0} that in the vapour. Then u_{p_0} being the specific volume of the liquid, and $v_{\pi_{0p_0}}$ that of the vapour at the corresponding pressures, we have

$$dp_0 = -g \frac{dh}{u_{p_0}}, \quad d\pi_{0p_0} = -g \frac{dh}{v_{\pi_{0p_0}}},$$

whence

$$\frac{\partial \pi_{0p_0}}{\partial p_0} = \frac{u_{p_0}}{v_{\pi_{0p_0}}}.$$

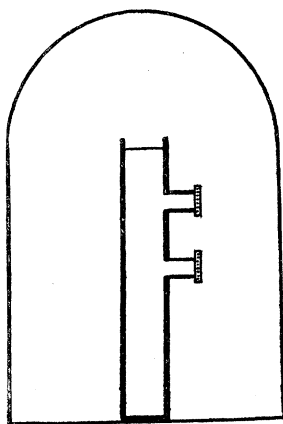


FIG. 2.

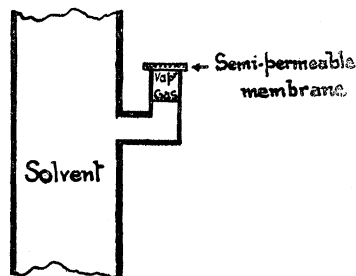


FIG. 3.

The semi-permeable membranes may be in direct contact with the liquid, or they may be separated from it by a space containing the vapour and an indifferent gas (see fig. 3).

This method is not applicable to the case of the vapour of a solution, because the concentration of the solution changes with the height. In this case,

$$\frac{dp}{dh} = -g\rho_p, \quad \frac{d\pi_p}{dh} = -\frac{g}{v_{\pi_p}}, \quad \frac{d\pi_p}{dh} = \left(\frac{\partial \pi_p}{\partial c}\right)_p \frac{dc}{dh} + \left(\frac{\partial \pi_p}{\partial p}\right)_c \frac{dp}{dh},$$

whence

$$\left(\frac{\partial \pi_p}{\partial c}\right)_p \frac{dc}{dh} = -g \left(\frac{1}{v_{\pi_p}} - \frac{\partial \pi_p}{\partial p} \rho_p \right).$$

Making use of the values obtained previously in this paper, some interesting results can, however, be obtained. We have

$$\frac{\partial \pi_p}{\partial p} = \frac{s_p}{v_{\pi_p}}, \quad \rho_p = \frac{1}{\sigma_p},$$

and writing

$$(\partial V / \partial m_2)_{m_1} \equiv s_p',$$

$$\left(\frac{\partial \pi_p}{\partial c} \right)_p \frac{dc}{dh} = - \frac{g}{v_{\pi_p}} \left(1 - \frac{s_p}{\sigma_p} \right).$$

By means of equation (4) this may be written

$$\left(\frac{\partial \pi_p}{\partial c} \right)_p \frac{dc}{dh} = - \frac{gc}{v_{\pi_p}} \frac{s_p' - s_p}{s_p + cs_p'}.$$

In the same way, if the semi-permeable membranes are permeable only to the vapour of the solute, we have

$$\left(\frac{\partial \phi_p}{\partial c} \right)_p \cdot \frac{dc}{dh} = - \frac{g}{w_{\phi_p}} \left(1 - \frac{s_p'}{\sigma_p} \right) = - \frac{g}{w_{\pi_p}} \frac{s_p - s_p'}{s_p + cs_p'}.$$

It will be seen from these equations that if $s_p' = s_p$, then either

$$\left(\frac{\partial \pi_p}{\partial c} \right)_p = 0, \quad \text{or} \quad \frac{dc}{dh} = 0.$$

Now comparison with equation (6) shows that when $s_p' = s_p$ each is equal to σ_p . This can only occur when the densities of the two constituents are nearly alike.

In all such thermodynamic equations $\left(\frac{\partial \pi_p}{\partial c} \right)_p$ and $\frac{dc}{dh}$ appear together. It would seem to be impossible to separate them.

Summary of Results.

1. An exact equation is obtained for the connection between osmotic pressure and the vapour-pressures of a solution and a solvent for compressible solutions of any degree of concentration.

2. The mode of variation of the vapour-pressure of *each* solute with hydrostatic pressure is found. This is given for each by the same formula as if the other solutes were absent.

3. The result is extended to the case of any number of volatile constituents. When the hydrostatic pressure of the *solution* is that due alone to the vapours of its constituents the equation reduces to as simple a form as when the constituents are involatile.

4. The osmotic pressure is found to change with hydrostatic pressure according to the same formula as when the solute is involatile.

5. A very simple proof is given of the variation of the vapour-pressure of a pure liquid with hydrostatic pressure. This proof cannot be extended to the case of a solution owing to a space-variation of concentration being set up under the conditions of the proof.

Addendum.—Received February 20, 1908.

In a previous paper* I have given an exact formula for the increase of vapour-pressure of a liquid with the hydrostatic pressure to which the liquid is subjected. This variation actually occurs in several familiar phenomena which can, therefore, all be linked together under one head.

1. The first of these phenomena which I shall consider is that of the difference of vapour-pressure for a curved and that for a plane surface. Let π be the vapour-pressure at a plane surface of a simple liquid in contact with its own vapour alone, so that its hydrostatic pressure is also π ; let π' be the vapour-pressure of the same liquid when in the form of a drop of radius R , and let T be the surface-tension. Then the hydrostatic pressure of the liquid in the latter case is $\pi' + 2T/R$.

Now in the paper referred to I have shown that

$$d\pi_p/dp = u_p/v_{\pi_p},$$

where u_p is the specific volume of the liquid,

π_p „ vapour-pressure,

and v_{π_p} „ specific volume of the vapour at the pressure π_p .

Hence, treating the change as small, we have, approximately,

$$\frac{\pi' - \pi}{\pi' - \pi + 2T/R} = \frac{u_\pi}{v_\pi}, \quad \text{or} \quad \pi' - \pi = \frac{2T}{R} \cdot \frac{u_\pi}{v_\pi - u_\pi}.$$

This is Kelvin's formula, expressed, however, in terms of specific volumes instead of in terms of densities as usual.

It is clear that if the hydrostatic pressure at the flat surface were increased to an equal amount by superposing an atmosphere of an independent gas, the vapour-pressure at the curved surface would not be different from that at the plane surface.

2. The next phenomenon is that of the change of vapour-pressure due to imparting an electric charge of surface density σ . The usual formula is obtainable by substituting $-2\pi\sigma^2$ for $2T/R$. It follows, therefore, that the change of vapour-pressure in this case is also directly due to the change in hydrostatic pressure: it is unnecessary to invoke any recondite effect of the electrification upon the surface.

3. The difference in the vapour-pressure of a solution from that of the pure solvent, *when both are at the same hydrostatic pressure*, can also be attributed to the fact that the partial pressure of the solvent in the solution is then less than the total pressure. In making this statement, I regard the hydrostatic pressure p of the solution as made up of: (a) a partial pressure,

* 'Roy. Soc. Proc.,' A, vol. 79, 1907, p. 525.

1908.] *Compressible Solutions of any Concentration.* 465

equal to the osmotic pressure P due to the salt; (b) a partial pressure p_0 due to the solvent, so that $p - p_0 = P$. I must recall the fact that I have proved* that when a solution is in equilibrium with the pure solvent, the vapour-pressures of both are the same. That is to say, the vapour-pressure of a solution at a hydrostatic pressure p is the same as the vapour-pressure of the solvent under a hydrostatic pressure p_0 where these pressures differ by the amount P . So that, provided the partial pressure of the solvent is the same, the vapour-pressure is the same whether it is in a solution or not.

Conclusion.

I have thus considered several cases in which the vapour-pressure is changed, and found that in each case it is only necessary to know the partial pressure of the pure solvent whose vapour we refer to in order to calculate what the change in the vapour-pressure amounts to. The same method might presumably be applied to other cases also, such as magnetisation, etc. In this addendum the approximate formulæ only have been given, in order that comparison may be made at once with familiar formulæ. The exact forms can easily be written down when required.

* *Loc. cit.*, p. 526.
